

# MEAN AMPLITUDES OF VIBRATION OF SOME TRIGONAL BIPYRAMIDAL PENTACHLORIDES

G. NAGARAJAN\*

DEPARTMENT OF CHEMISTRY, OKLAHOMA STATE UNIVERSITY,  
STILLWATER, OKLAHOMA, U.S.A.

(Received January, 1963; Resubmitted February, 27 1964)

**ABSTRACT.** For the determination of the mean-square amplitudes of vibration of trigonal bipyramidal pentahalides a method has been developed by giving the symmetry coordinates properly constructed and oriented, kinetic energy matrices, mean-square amplitude matrices, analytical expressions for all the possible mean-square amplitude quantities and secular equations for the normal frequencies. This method has been applied to determine the mean amplitudes of vibration for the pentachlorides of phosphorous, antimony and molybdenum at the temperatures  $T = 0$  and  $T = 298^\circ\text{K}$  respectively.

## INTRODUCTION

In the solid, liquid and vapour phase the Raman spectrum of phosphorous pentachloride was obtained by Krishnamurthi (1930) and Moureu, Magat and Wetroff (1937). Rouault (1940) and Sargent and Schomaker (1941) by their electron diffraction investigations and Pauling (1942) by his theoretical explanation established that phosphorous pentachloride has a trigonal bipyramidal structure with the symmetry point group  $D_{3h}$ . Using the then available Raman data, Siebert (1951) made a vibrational assignment on the basis of the above structure. Haarhoff and Pistorius (1959), on the basis of Wilson's group theoretical method (1939 and 1941) calculated the force constants without the two fundamental frequencies coming under the  $A_2''$  species in addition to other similar molecules. Recently Wilmshurst and Bernstein (1957) have studied the Raman as well as infrared spectra of  $\text{PCl}_5$  in the liquid and gaseous states, assigned all the fundamental frequencies with a simple normal coordinate treatment and calculated the molar thermodynamic functions.

The Raman spectrum of antimony pentachloride was studied by Keirz and Stricks (1937), Moureu, Magat and Wetroff (1938) and Moureu, Sue and Magat (1947-1948). Rouault (1940) by his electron diffraction data in the gaseous state and Ohlberg (1954) by his X-ray diffraction measurements in the solid state confirmed the  $D_{3h}$  symmetry for  $\text{SbCl}_5$ . With the help of the existing Raman data, Siebert (1951) attempted a vibrational assignment on the basis of  $D_{3h}$  symmetry. Recently, Wilmshurst (1960) has studied the infrared absorption

---

\* At present Department of Chemistry, University of Maryland, U. S. A.

spectrum in the gaseous state, assigned all the fundamental frequencies and then calculated the thermodynamic functions by the statistical method.

The Raman spectrum of niobium pentachloride was studied by Moureu, Magat and Wettruff (1938) and Moureu, Magat and Sue (1947-1948). Skinner and Sutton (1940) carried out an electron diffraction study and confirmed the trigonal bipyramidal structure for  $\text{NbCl}_5$ . Recently, Gaunt, and Ainscough (1957) have studied the Raman and infrared absorption spectra of this molecule and assigned all the fundamental frequencies on the basis of  $D_{3h}$  symmetry. Nagarajan (1962) has calculated the molar thermodynamic functions of this molecule after giving a detailed procedure for the calculation of these functions.

It is the aim of the present investigation to give a method for the determination of the mean-square amplitudes of vibration of trigonal bipyramidal  $\text{XY}_5$  type molecules following the principle outlined by Cyvin (1959) and then to apply for the computation of the mean-square amplitudes of vibration of  $\text{PCl}_5$ ,  $\text{SbCl}_5$  and  $\text{NbCl}_5$  from their vibrational spectral data at the temperatures  $T' = 0$  and  $T' = -298^\circ\text{K}$  respectively.

#### SYMMETRY COORDINATES

The trigonal bipyramidal pentahalides with the symmetry point group  $D_{3h}$  give rise to the following fundamental frequencies under the various irreducible representations:  $2A_1'(R, p) + 2A_2''(I, \perp) + 3E'(R, dp; I, \perp) + E''(R, dp)$  where  $R$ ,  $I$ ,  $p$ ,  $dp$ ,  $\parallel$  and  $\perp$  stand for Raman active, infrared active, polarized, depolarized parallel and perpendicular respectively. Two normal modes of vibration under the  $A_1'$  species, one under the  $A_2''$  species and one under the  $E'$  species have been

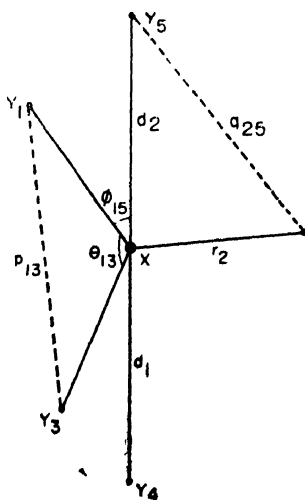


Fig. 1. The internal coordinates for the trigonal bipyramidal  $\text{XY}_5$  type molecule. The symbols denote deviations from the equilibrium distances and angles.

associated with essentially valency vibrations and the remaining with essentially deformation vibrations. The harmonic vibrations of the  $XY_6$  type molecule have been described by fourteen internal coordinates (Fig. 1). With the help of these internal coordinates the following set of symmetry coordinates satisfying the conditions of normalization, orthogonality and transformations of the concerned vibration species has been constructed :

$$\begin{aligned}
 S_1(A_1') &= (3)^{-\frac{1}{2}}(r_1 + r_2 + r_3) \\
 S_2(A_1') &= (2)^{-\frac{1}{2}}(d_1 + d_2) \\
 S_3(A_2'') &= (2)^{-\frac{1}{2}}(d_1 - d_2) \\
 S_4(A_2'') &= (RD)^{\frac{1}{2}}(6)^{-\frac{1}{2}}(\phi_{14} + \phi_{24} + \phi_{34} - \phi_{15} - \phi_{25} - \phi_{35}) \\
 S_{5a}(E') &= (6)^{-\frac{1}{2}}(2r_1 - r_2 - r_3) \\
 S_{5b}(E') &= (2)^{-\frac{1}{2}}(r_2 - r_3) \\
 S_{6a}(E') &= R(6)^{-\frac{1}{2}}(2\theta_{23} - \theta_{12} - \theta_{13}) \\
 S_{6b}(E') &= R(2)^{-\frac{1}{2}}(\theta_{12} - \theta_{13}) \\
 S_{7a}(E') &= (RD)^{\frac{1}{2}}(12)^{-\frac{1}{2}}(2\phi_{11} - \phi_{24} - \phi_{34} - 2\phi_{15} - \phi_{25} - \phi_{35}) \\
 S_{7b}(E') &= (RD)^{\frac{1}{2}}(\phi_{24} - \phi_{34} + \phi_{25} - \phi_{35})/2 \\
 S_{8a}(E') &= (RD)^{\frac{1}{2}}(12)^{-\frac{1}{2}}(2\phi_{14} - \phi_{24} - \phi_{34} - 2\phi_{15} + \phi_{25} + \phi_{35}) \\
 S_{8b}(E') &= (RD)^{\frac{1}{2}}(\phi_{24} - \phi_{34} - \phi_{25} + \phi_{35})/2 \\
 S_{r1} &= R(3)^{-\frac{1}{2}}(\theta_{12} + \theta_{23} + \theta_{13}) = 0 \text{ (Redundant)} \\
 S_{r2} &= (RD)^{\frac{1}{2}}(6)^{-\frac{1}{2}}(\phi_{14} + \phi_{24} + \phi_{34} + \phi_{15} + \phi_{25} + \phi_{35}) = 0 \text{ (Redundant)}
 \end{aligned}$$

It should be noticed that the angle displacements have been multiplied by the equilibrium bond lengths  $R$  and  $D$  in order to maintain the same dimensions for the various mean-square amplitude quantities.

#### KINETIC ENERGY MATRICES

Following the methods outlined by Wilson (1939, 1941), the symmetrized  $G$  and  $G^{-1}$  matrices have been obtained for the various irreducible representations as follows :

$G_{11}(A_1') = \mu_y$	$G_{11}^{-1}(A_1') = \mu_y^{-1}$
$G_{22}(A_1') = \mu_y$	$G_{22}^{-1}(A_1') = \mu_y^{-1}$
$G_{12}(A_1') = G_{21}(A_1') = 0$	$G_{12}^{-1}(A_1') = G_{21}^{-1}(A_1') = 0$
$G_{33}(A_2'') = 2\mu_x + \mu_y$	$G_{33}^{-1}(A_2'') = (3\mu_x + \mu_y)(5\mu_x + \mu_y)^{-1}\mu_y^{-1}$
$G_{44}(A_2'') = 6\mu_x + 2\mu_y$	$G_{44}^{-1}(A_2'') = \frac{1}{2}(2\mu_x + \mu_y)(5\mu_x + \mu_y)^{-1}\mu_y^{-1}$
$G_{34}(A_2'') = G_{43}(A_2'') = (12)^{\frac{1}{2}}\mu_x$	$G_{34}^{-1}(A_2'') = G_{43}^{-1}(A_2'')$ $= 3^{\frac{1}{2}}\mu_x(5\mu_x + \mu_y)^{-1}\mu_y^{-1}$
$G_{55}(E') = (3/2)\mu_x + \mu_y$	$G_{55}^{-1}(E') = 3(\mu_x + \frac{1}{2}\mu_y)/K$

$$\begin{aligned}
G_{66}(E') &= (9/2)\mu_x + 3\mu_y & G_{66}^{-1}(E') &= \{(\mu_x + \frac{1}{2}\mu_y) - \frac{1}{2}\mu_x^2\}/K \\
G_{77}(E') &= 3\mu_x + (3/2)\mu_y & G_{77}^{-1}(E') &= (3\mu_x + 2\mu_y)/2K \\
G_{56}(E') &= G_{65}(E') = 0 & G_{65}^{-1}(E') &= G_{56}^{-1}(E') = 0 \\
G_{57}(E') &= G_{75}(E') = -(3/2)\mu_x & G_{57}^{-1}(E') &= G_{75}^{-1}(E') = (3/2)\mu_x \\
G_{67}(E') &= G_{76}(E') = 0 & G_{67}^{-1}(E') &= G_{76}^{-1}(E') = 0 \\
G_{88}(E'') &= (7/2)\mu_y & G_{88}^{-1}(E'') &= (2/7)\mu_y^{-4} \\
\text{Here } K &= (3/2)\{(3\mu_x + 2\mu_y)(\mu_x + \frac{1}{2}\mu_y) - \mu_x^2\}
\end{aligned}$$

where  $\mu_x$  and  $\mu_y$  are the reciprocal masses of the X and Y atoms respectively.

#### MEAN-SQUARE AMPLITUDE MATRICES

Following the methods outlined by Cyvin (1959), the symmetrized mean-square amplitude matrices  $\Sigma$  have been obtained by introducing the symmetry coordinates as follows :

$$\begin{aligned}
\Sigma_{11}(A'_1) &= \langle S_1^2 \rangle = \sigma_r + 2\sigma_{rr} \\
\Sigma_{22}(A'_1) &= \langle S_2^2 \rangle = \sigma_d + \sigma_{dd} \\
\Sigma_{12}(A'_1) &= \Sigma_{21}(A'_1) = \langle S_1 S_2 \rangle = (6)^{1/2} \sigma_{rd} \\
\Sigma_{33}(A''_2) &= \langle S_3^2 \rangle = \sigma_d - \sigma_{dd} \\
\Sigma_{44}(A''_2) &= \langle S_4^2 \rangle = \sigma_\varphi - \sigma_{\varphi\varphi} + 2\sigma'_{\varphi\varphi} - 2\sigma''_{\varphi\varphi} \\
\Sigma_{34}(A''_2) &= \Sigma_{43}(A''_2) = \langle S_3 S_4 \rangle = (3)^{1/2} (\sigma_{d\varphi} - \sigma'_{\varphi\varphi}) \\
\Sigma_{55}(E') &= \langle S_{5a}^2 \rangle = \langle S_{5b}^2 \rangle = \sigma_r - \sigma_{rr} \\
\Sigma_{66}(E') &= \langle S_{6a}^2 \rangle = \langle S_{6b}^2 \rangle = \sigma_\theta - \sigma_{\theta\theta} \\
\Sigma_{77}(E') &= \langle S_{7a}^2 \rangle = \langle S_{7b}^2 \rangle = \sigma_\varphi + \sigma_{\varphi\varphi} - \sigma'_{\varphi\varphi} - \sigma''_{\varphi\varphi} \\
\Sigma_{56}(E') &= \Sigma_{65}(E') = \langle S_{5a} S_{6a} \rangle = \langle S_{5b} S_{6b} \rangle = \sigma_{r\theta} - \sigma'_{r\theta} \\
\Sigma_{57}(E') &= \Sigma_{75}(E') = \langle S_{57} S_{7a} \rangle = \langle S_{6b} S_{7b} \rangle = (2)^{1/2} (\sigma_{r\varphi} - \sigma'_{r\varphi}) \\
\Sigma_{67}(E') &= \Sigma_{76}(E') = \langle S_{6a} S_{7a} \rangle = \langle S_{6b} S_{7b} \rangle = (2)^{1/2} (\sigma_{\theta\varphi} - \sigma_{\theta\varphi}) \\
\Sigma_{88}(E'') &= \langle S_{8a}^2 \rangle = \langle S_{8b}^2 \rangle = \sigma_\varphi - \sigma_{\varphi\varphi} - \sigma'_{\varphi\varphi} + \sigma''_{\varphi\varphi}
\end{aligned}$$

where the entering quantities have been defined by the mean values given in the following :

$$\begin{aligned}
\sigma_r &= \langle r_1^2 \rangle = \langle r_2^2 \rangle = \langle r_3^2 \rangle \\
\sigma_{rr} &= \langle r_1 r_2 \rangle = \langle r_1 r_3 \rangle = \langle r_2 r_3 \rangle \\
\sigma_d &= \langle d_1^2 \rangle = \langle d_2^2 \rangle \\
\sigma_{dd} &= \langle d_1 d_2 \rangle \\
\sigma_{rd} &= \langle r_1 d_1 \rangle = \langle r_2 d_1 \rangle = \langle r_3 d_1 \rangle = \langle r_1 d_2 \rangle = \langle r_2 d_2 \rangle = \langle r_3 d_2 \rangle \\
\sigma_\theta &= R^2 \langle \theta_{12}^2 \rangle = R^2 \langle \theta_{23}^2 \rangle = R^2 \langle \theta_{13}^2 \rangle
\end{aligned}$$

$$\begin{aligned}
 \sigma_{\theta\theta} &= R^2 \langle \theta_{12} \theta_{23} \rangle = R^2 \langle \theta_{12} \theta_{13} \rangle = R^2 \langle \theta_{23} \theta_{13} \rangle \\
 \sigma'_{\varphi} &= RD \langle \phi_{14}^2 \rangle = RD \langle \phi_{24}^2 \rangle = RD \langle \phi_{34}^2 \rangle = RD \langle \phi_{15}^2 \rangle = RD \langle \phi_{25}^2 \rangle \\
 &= RD \langle \phi_{35}^2 \rangle \\
 \sigma_{\varphi\varphi} &= RD \langle \phi_{14} \phi_{15} \rangle = RD \langle \phi_{24} \phi_{35} \rangle = RD \langle \phi_{34} \phi_{35} \rangle \\
 \sigma'_{\varphi\varphi} &= RD \langle \phi_{14} \phi_{24} \rangle = RD \langle \phi_{14} \phi_{34} \rangle = RD \langle \phi_{24} \phi_{34} \rangle = RD \langle \phi_{15} \phi_{25} \rangle \\
 &= RD \langle \phi_{15} \phi_{35} \rangle = RD \langle \phi_{25} \phi_{35} \rangle \\
 \sigma''_{\varphi\varphi} &= RD \langle \phi_{14} \phi_{25} \rangle = RD \langle \phi_{14} \phi_{35} \rangle = RD \langle \phi_{24} \phi_{15} \rangle = RD \langle \phi_{24} \phi_{35} \rangle \\
 &= RD \langle \phi_{34} \phi_{15} \rangle = RD \langle \phi_{34} \phi_{25} \rangle \\
 \sigma_{d\varphi} &= (RD)^{\frac{1}{2}} \langle d_1 \phi_{14} \rangle = (RD)^{\frac{1}{2}} \langle d_1 \phi_{24} \rangle = (RD)^{\frac{1}{2}} \langle d_1 \phi_{34} \rangle = (RD)^{\frac{1}{2}} \langle d_2 \phi_{15} \rangle \\
 &= (RD)^{\frac{1}{2}} \langle d_2 \phi_{25} \rangle = (RD)^{\frac{1}{2}} \langle d_2 \phi_{35} \rangle \\
 \sigma'_{d\varphi} &= (RD)^{\frac{1}{2}} \langle d_1 \phi_{15} \rangle = (RD)^{\frac{1}{2}} \langle d_1 \phi_{25} \rangle = (RD)^{\frac{1}{2}} \langle d_1 \phi_{35} \rangle = (RD)^{\frac{1}{2}} \langle d_2 \phi_{14} \rangle \\
 &= (RD)^{\frac{1}{2}} \langle d_2 \phi_{24} \rangle = (RD)^{\frac{1}{2}} \langle d_2 \phi_{34} \rangle \\
 \sigma_{r\theta} &= R \langle r_1 \theta_{12} \rangle = R \langle r_1 \theta_{13} \rangle = R \langle r_2 \theta_{12} \rangle = R \langle r_2 \theta_{23} \rangle = R \langle r_3 \theta_{23} \rangle \\
 &= R \langle r_3 \theta_{13} \rangle \\
 \sigma_{r\theta}' &= R \langle r_1 \theta_{23} \rangle = R \langle r_2 \theta_{13} \rangle = R \langle r_3 \theta_{12} \rangle \\
 \sigma_{r\varphi} &= (RD)^{\frac{1}{2}} \langle r_1 \phi_{14} \rangle = (RD)^{\frac{1}{2}} \langle r_1 \phi_{15} \rangle = (RD)^{\frac{1}{2}} \langle r_2 \phi_{24} \rangle = (RD)^{\frac{1}{2}} \langle r_2 \phi_{25} \rangle \\
 &= (RD)^{\frac{1}{2}} \langle r_3 \phi_{34} \rangle = (RD)^{\frac{1}{2}} \langle r_3 \phi_{35} \rangle \\
 \sigma'_{r\varphi} &= (RD)^{\frac{1}{2}} \langle r_1 \phi_{24} \rangle = (RD)^{\frac{1}{2}} \langle r_1 \phi_{34} \rangle = (RD)^{\frac{1}{2}} \langle r_1 \phi_{25} \rangle = (RD)^{\frac{1}{2}} \langle r_1 \phi_{35} \rangle \\
 &= (RD)^{\frac{1}{2}} \langle r_2 \phi_{14} \rangle = (RD)^{\frac{1}{2}} \langle r_2 \phi_{34} \rangle = (RD)^{\frac{1}{2}} \langle r_2 \phi_{15} \rangle = (RD)^{\frac{1}{2}} \langle r_2 \phi_{35} \rangle \\
 &= (RD)^{\frac{1}{2}} \langle r_3 \phi_{14} \rangle = (RD)^{\frac{1}{2}} \langle r_3 \phi_{24} \rangle = (RD)^{\frac{1}{2}} \langle r_3 \phi_{15} \rangle = (RD)^{\frac{1}{2}} \langle r_3 \phi_{25} \rangle \\
 \sigma_{\theta\varphi} &= (R^3 D)^{\frac{1}{2}} \langle \theta_{12} \phi_{14} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{12} \phi_{24} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{12} \phi_{15} \rangle \\
 &= (R^3 D)^{\frac{1}{2}} \langle \theta_{12} \phi_{25} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{23} \phi_{24} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{23} \phi_{34} \rangle \\
 &= (R^3 D)^{\frac{1}{2}} \langle \theta_{23} \phi_{25} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{23} \phi_{35} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{13} \phi_{14} \rangle \\
 &= (R^3 D)^{\frac{1}{2}} \langle \theta_{13} \phi_{34} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{13} \phi_{15} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{13} \phi_{35} \rangle \\
 \sigma'^{\theta}_{\varphi} &= (R^3 D)^{\frac{1}{2}} \langle \theta_{12} \phi_{34} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{12} \phi_{35} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{23} \phi_{14} \rangle \\
 &= (R^3 D)^{\frac{1}{2}} \langle \theta_{23} \phi_{15} \rangle \\
 &= (R^3 D)^{\frac{1}{2}} \langle \theta_{13} \phi_{24} \rangle = (R^3 D)^{\frac{1}{2}} \langle \theta_{13} \phi_{25} \rangle
 \end{aligned}$$

Some linear combinations of the above mean-square amplitude quantities have become zero due to the construction of two redundant coordinates in this case. From the well-known relations

$$\langle S_r^2 \rangle = 0; \quad \langle S_r S_i \rangle = 0$$

where  $S_r$  is the redundant coordinate and  $S_i$  an arbitrary coordinate, it has been found

$$\begin{aligned}
 \sigma_{\theta} + 2\sigma_{\theta\theta} &= 0 \\
 \sigma_{\varphi} + \sigma_{\varphi\varphi} + 2\sigma'_{\varphi\varphi} + 2\sigma''_{\varphi\varphi} &= 0
 \end{aligned}$$

$$2\sigma_{r\theta} + \sigma'_{r\theta} = 0$$

$$\sigma_{d\theta} = 0$$

$$\sigma_{r\varphi} + 2\sigma'_{r\varphi} = 0$$

$$\sigma_{d\varphi} + \sigma'_{d\varphi} = 0$$

$$2\sigma_{\theta\varphi} + \sigma'_{\theta\varphi} = 0$$

### NORMAL FREQUENCIES

From the secular equations  $|\Sigma G^{-1} - E\Delta| = 0$  set up by Cyvin (1959), the following set of equations for the normal frequencies containing the symmetrized mean-square amplitude matrix elements has been derived :

$$\Delta_1 + \Delta_2 = \Sigma_{11} G_{11}^{-1} + \Sigma_{22} G_{22}^{-1}$$

$$\Delta_1 \Delta_2 = (\Sigma_{11} \Sigma_{22} - \Sigma_{12}^2) (G_{11}^{-1} G_{22}^{-1})$$

$$\Delta_3 + \Delta_4 = \Sigma_{33} G_{33}^{-1} + \Sigma_{44} G_{44}^{-1} + 2\Sigma_{34} G_{34}^{-1}$$

$$\Delta_3 \Delta_4 = (\Sigma_{33} \Sigma_{44} - \Sigma_{34}^2) (G_{33}^{-1} G_{44}^{-1} - G_{34}^{-12})$$

$$\Delta_5 + \Delta_6 + \Delta_7 = \Sigma_{55} G_{55}^{-1} + \Sigma_{66} G_{66}^{-1} + \Sigma_{77} G_{77}^{-1} + 2\Sigma_{57} G_{57}^{-1}$$

$$\Delta_5 \Delta_6 + \Delta_5 \Delta_7 + \Delta_6 \Delta_7 = (\Sigma_{55} \Sigma_{66} - \Sigma_{56}^2) G_{55}^{-1} G_{66}^{-1} + (\Sigma_{55} \Sigma_{77} - \Sigma_{57}^2) (G_{55}^{-1} G_{66}^{-1} - G_{57}^{-12}) \\ + (\Sigma_{66} \Sigma_{77} - \Sigma_{67}^2) (G_{66}^{-1} G_{77}^{-1} - 2(\Sigma_{56} \Sigma_{67} - \Sigma_{66} \Sigma_{57}) G_{66}^{-1} G_{57}^{-1})$$

$$\Delta_5 \Delta_6 \Delta_7 = (\Sigma_{55} \Sigma_{66} \Sigma_{77} - \Sigma_{55} \Sigma_{67}^2 - \Sigma_{66} \Sigma_{57}^2 - \Sigma_{77} \Sigma_{56}^2 + 2\Sigma_{56} \Sigma_{57} \Sigma_{67}) \\ (G_{55}^{-1} G_{66}^{-1} - G_{77}^{-1} G_{66}^{-1} G_{57}^{-12})$$

$$\Delta_8 = \Sigma_{88} G_{88}^{-1}$$

$\Delta$  in the above equations has been related to the normal frequency  $\nu$  as

$$\Delta_i = (h/8\pi^2 \nu_i) \coth(h\nu_i/2KT)$$

where  $\kappa$  is the Boltzmann constant and  $T$  the temperature in degrees Kelvin.

### ADDITIONAL MEAN-SQUARE AMPLITUDE QUANTITIES

The interatomic distance displacements between the non-bonded atom pairs, instead of the angle derivations, have been taken into account and designated as  $p_{12}$ ,  $p_{23}$ ,  $p_{13}$ ,  $q_{15}$ ,  $q_{25}$  and  $q_{35}$  (Fig. 1). Then the following additional mean square amplitude quantities have been obtained :

$$\sigma_p = \langle p_{12}^2 \rangle = \langle p_{23}^2 \rangle = \langle p_{13}^2 \rangle$$

$$\sigma_{pp} = \langle p_{12} p_{23} \rangle = \langle p_{12} p_{13} \rangle = \langle p_{23} p_{13} \rangle$$

$$\sigma_q = \langle q_{14}^2 \rangle = \langle q_{24}^2 \rangle = \langle q_{34}^2 \rangle = \langle q_{15}^2 \rangle = \langle q_{25}^2 \rangle = \langle q_{35}^2 \rangle$$

$$\sigma_{qq} = \langle q_{14} q_{24} \rangle = \langle q_{14} q_{34} \rangle = \langle q_{24} q_{34} \rangle = \langle q_{15} q_{25} \rangle \\ = \langle q_{15} q_{35} \rangle = \langle q_{25} q_{35} \rangle$$

$$\sigma'_{qq} = \langle q_{14} q_{15} \rangle = \langle q_{24} q_{25} \rangle = \langle q_{34} q_{35} \rangle$$

$$\sigma''_{qq} = \langle q_{14} q_{25} \rangle = \langle q_{14} q_{35} \rangle = \langle q_{24} q_{35} \rangle = \langle q_{24} q_{15} \rangle - \langle q_{34} q_{15} \rangle \\ = \langle q_{34} q_{25} \rangle$$

$$\sigma_{pq} = \langle p_{12} q_{14} \rangle = \langle p_{12} q_{24} \rangle = \langle p_{12} q_{15} \rangle = \langle p_{12} q_{25} \rangle = \langle p_{23} q_{24} \rangle \\ = \langle p_{23} q_{34} \rangle = \langle p_{23} q_{25} \rangle = \langle p_{23} q_{35} \rangle = \langle p_{13} q_{34} \rangle = \langle p_{13} q_{14} \rangle \\ = \langle p_{13} q_{35} \rangle = \langle p_{13} q_{15} \rangle$$

$$\sigma'_{pq} = \langle p_{12} q_{34} \rangle = \langle p_{12} q_{35} \rangle = \langle p_{23} q_{14} \rangle = \langle p_{23} q_{15} \rangle = \langle p_{13} q_{24} \rangle \\ = \langle p_{13} q_{25} \rangle$$

The above additional mean-square amplitude quantities defined by the mean values of the deviations of the bonded as well as non-bonded distances are not independent of the mean-square amplitude quantities previously defined in one of the sections of this article by the mean values of the deviations of the interbond distances and interbond angles. All these quantities, in fact, may well be expressed analytically in terms of the symmetrized mean-square amplitude matrix elements  $\Sigma$ . If one of the introduced internal coordinates ( $\epsilon_1$ ) —  $r, d, R\theta$  or  $(RD)^{1/2}\phi$  has been given in terms of the symmetry coordinates by

$$\epsilon_i = \sum_k A_{ik} S_k$$

it has been found

$$\langle \epsilon_i \epsilon_j \rangle = \sum_k \sum_l A_{ik} A_{jl} \Sigma_{kl},$$

where  $\Sigma_{kl}$  denotes the elements of the  $\Sigma$  matrix. The mean-square amplitude quantities in terms of the symmetrized mean-square amplitude matrix elements  $\Sigma$  have been obtained as follows :

$$\begin{aligned} \sigma_r &= (1/3)(\Sigma_{11} + 2\Sigma_{55}) \\ \sigma_{rr} &= (1/3)(\Sigma_{11} - \Sigma_{55}) \\ \sigma_d &= (1/2)(\Sigma_{22} + \Sigma_{33}) \\ \sigma_{dd} &= (1/2)(\Sigma_{22} - \Sigma_{33}) \\ \sigma_{rd} &= (6)^{-1/2}\Sigma_{12} \\ \sigma_\theta &= (2/3)\Sigma_{66} \\ \sigma_{\theta\theta} &= -(1/3)\Sigma_{66} \\ \sigma_\phi &= (1/4)\Sigma_{44} + (5/12)\Sigma_{77} + (1/4)\Sigma_{88} \\ \sigma_{\phi\phi} &= -(1/4)\Sigma_{44} + (1/4)\Sigma_{77} - (1/4)\Sigma_{88} \\ \sigma'_{\phi\phi} &= (1/4)\Sigma_{44} - (1/12)\Sigma_{77} - (1/4)\Sigma_{88} \\ \sigma''_{\phi\phi} &= -(1/4)\Sigma_{44} - (1/4)\Sigma_{77} + (1/4)\Sigma_{88} \\ \sigma_{d\phi} &= (12)^{-1/2}\Sigma_{34} \end{aligned}$$

$$\begin{aligned}
\sigma'_{d\phi} &= -(12)^{-1}\Sigma_{34} \\
\sigma_{r\phi} &= (2/9)^{1/2}\Sigma_{67} \\
\sigma'_{r\phi} &= -(18)^{-1}\Sigma_{57} \\
\sigma_{r\theta} &= (1/3)\Sigma_{56} \\
\sigma'_{r\theta} &= -(2/3)\Sigma_{56} \\
\sigma_p &= \Sigma_{11} + (1/2)\Sigma_{55} + (1/6)\Sigma_{66} - (3)^{-1}\Sigma_{56} \\
\sigma_{pp} &= \Sigma_{11} - (1/4)\Sigma_{55} - (1/12)\Sigma_{66} + (12)^{-1/2}\Sigma_{56} \\
\sigma_q &= (1/6)\Sigma_{11} + (1/4)\Sigma_{22} + (1/4)\Sigma_{33} + (1/12)\Sigma_{44} + (1/3)\Sigma_{55} + (1/6)\Sigma_{77} \\
&\quad + (1/6)\Sigma_{88} + (6)^{-1/2}\Sigma_{12} + (12)^{-1/2}\Sigma_{34} + (2/9)^{1/2}\Sigma_{57} \\
\sigma_{qq} &= (1/6)\Sigma_{11} + (1/4)\Sigma_{22} + (1/4)\Sigma_{33} + (1/12)\Sigma_{44} - (1/6)\Sigma_{55} - (1/12)\Sigma_{77} - (1/12)\Sigma_{88} \\
&\quad + (6)^{-1/2}\Sigma_{12} + (12)^{-1/2}\Sigma_{34} - (18)^{1/2}\Sigma_{57} \\
\sigma'_{qq} &= (1/6)\Sigma_{11} + (1/4)\Sigma_{22} - (1/4)\Sigma_{33} - (1/12)\Sigma_{44} + (1/3)\Sigma_{55} + (1/6)\Sigma_{77} - (1/6)\Sigma_{88} \\
&\quad + (6)^{-1/2}\Sigma_{12} - (12)^{-1/2}\Sigma_{34} + (2/9)R\Sigma_{57} \\
\sigma''_{qq} &= (1/6)\Sigma_{11} + (1/4)\Sigma_{22} - (1/4)\Sigma_{33} - (1/12)\Sigma_{44} - (1/6)\Sigma_{55} - (1/12)\Sigma_{77} \\
&\quad + (1/12)\Sigma_{88} + (6)^{-1/2}\Sigma_{12} - (12)^{-1/2}\Sigma_{34} - (18)^{-1/2}\Sigma_{57} \\
\sigma_{pq} &= (6)^{-1/2}\Sigma_{11} + (24)^{-1/2}\Sigma_{55} + (1/2)\Sigma_{12} - (72)^{-1/2}\Sigma_{56} + (48)^{-1/2}\Sigma_{57} - (1/12)\Sigma_{67} \\
\sigma'_{pq} &= (6)^{-1/2}\Sigma_{11} - (6)^{-1/2}\Sigma_{55} + (1/2)\Sigma_{12} + (18)^{-1/2}\Sigma_{56} - (12)^{-1/2}\Sigma_{57} + (1/6)\Sigma_{67}
\end{aligned}$$

It should be noticed that all of the mean-square amplitude quantities defined in the previous section appear in the symmetrized mean-square amplitude matrix elements except  $\sigma_{d\theta}$ . This becomes vanished by symmetry of the molecular system.

## RESULTS

The fundamental frequencies in  $\text{cm}^{-1}$  for  $\text{PCl}_5$  given by Wilmschurst and Bernstein (1957), for  $\text{SbCl}_5$  by Wilmschurst (1960) and for  $\text{NbCl}_5$  by Gaunt and Ainscough (1957) have been given in Table I. The secular equations giving the normal frequencies in terms of the mean-square amplitudes of vibration were constructed with the help of the fundamental frequencies  $\Sigma$  and  $G^{-1}$  matrices and then solved. Since it is not possible to solve all the symmetrized mean-square amplitude matrices uniquely, most of the non-diagonal terms were neglected for the sake of simplicity in the evaluation. In fact, the magnitude of many non-diagonal terms is effectively negligible in comparing that of the diagonal elements and the contribution of these toward the mean-square amplitude quantities is not much significant. The evaluated symmetrized mean-square amplitude matrices in  $\text{\AA}^2$  for the three molecules at the temperatures  $T = 0$  and  $T = 298^\circ\text{K}$  have been given in Tables II, III and IV respectively. The computed numerical



values of the mean-square amplitude quantities in  $\text{\AA}^2$  at these temperatures have been given in Tables V, VI and VII respectively where  $\sigma_r$  is the mean-square amplitude quantity due to the bonded atom pair  $X-Y$  in the girdle,  $\sigma_{rr}$  the quantity due to the interaction of two bonded atom pairs in the girdle,  $\sigma_d$  the quantity due to the bonded atom pair in the symmetry axis,  $\sigma_{dd}$  the interaction term due to two bonded atom pairs in the symmetry axis,  $\sigma_\theta$  the quantity due to the bending  $Y-X-Y$  in the equatorial plane,  $\sigma_\varphi$  the quantity due to the bending  $Y(\text{equatorial})-X-Y(\text{axial})$ ,  $\sigma_p$  the quantity due to the nonbonded atom pair  $Y-Y$  in the equatorial plane,  $\sigma_q$  the quantity due to the nonbonded atom pair  $Y(\text{equatorial})-Y(\text{axial})$  and  $\sigma_{\theta\theta}$ ,  $\sigma_{\varphi\varphi}$ ,  $\sigma'_{\varphi\varphi}$ ,  $\sigma''_{\varphi\varphi}$ ,  $\sigma_{d\varphi}$ ,  $\sigma'_{r\varphi}$ ,  $\sigma_{rc}$ ,  $\sigma'_{r\varphi}$ ,  $\sigma_{pp}$ ,  $\sigma_{qq}$ ,  $\sigma'_{qq}$ ,  $\sigma''_{qq}$ ,  $\sigma_{pq}$  and  $\sigma'_{pq}$  are the respective interaction terms. The corresponding mean amplitudes of vibration in  $\text{\AA}$  for the bonded as well as nonbonded atom pairs have been reported in Table VIII for all the three molecules at the two temperatures.

It has been observed for all the three molecules that many of the interaction quantities due to the bonded distances, non-bonded distances and bendings of the molecule are significantly small (Tables V, VI and VII).

The mean-square amplitude quantity due to the bending  $Y-X-Y$  in the equatorial plane is always less than that of the bending  $Y(\text{equatorial})-X-Y(\text{axial})$  (Tables V, VI and VII).

The mean amplitudes of vibration for the bonded (axial) atom pairs are very similar to those of the bonded (equatorial) atom pairs. (Table VIII).

The mean amplitudes of vibration for the nonbonded (equatorial-axial) atom pairs are greater than those of the non bonded (equatorial-equatorial) atom pairs. (Table VIII).

The mean amplitudes of vibration for the nonbonded atom pairs are in general greater than those of the bonded atom pairs.

In general, for any molecule, if the fundamental frequencies in wave numbers are greater than  $1200\text{ cm}^{-1}$ , the hyperbolic cotangent differs very little from unity for the temperatures near  $298^\circ\text{K}$  i.e.  $\coth(h\nu/2KT) \approx 1$  and the consequent effect is that the mean-square amplitude of vibration is an independent function of temperature. If, on the other hand, the fundamental frequencies in wave numbers are less than  $200\text{ cm}^{-1}$ , the value of the coth function is not so accurate but merely approximate for the temperatures near  $298^\circ\text{K}$  and correspondingly the mean-square amplitude of vibration is a dependent function of temperature. In fact, in each molecule of the present investigation most of the fundamental frequencies fall between  $600\text{ cm}^{-1}$  and  $200\text{ cm}^{-1}$  except a few which may not seriously affect the calculations. Hence, the obtained values of the mean amplitudes of vibration for all the three molecules are the most probable and reliable ones.

TABLE I

Fundamental frequencies in  $\text{cm}^{-1}$  for some trigonal bipyramidal pentachlorides

Symmetry species	vibration	$\text{PCl}_5$	$\text{SbCl}_5$	$\text{NbCl}_5$
$A'_1$	$\nu_1$	394	356	412
	$\nu_2$	394	307	355
$A''_2$	$\nu_3$	465	384	315
	$\nu_4$	176	156	260
	$\nu_5$	592	398	497
$E'$	$\nu_6$	335	182	396
	$\nu_7$	100	74	106
$E''$	$\nu_8$	280	166	153

TABLE II

Symmetrized mean-square amplitude matrices in  $\text{\AA}^2$  for phosphorous pentachloride

Element	Symmetrized mean-square amplitude matrix	
	$T = 0$	$T = 298^\circ\text{K}$
$\Sigma_{11}$	0.0012071	0.0016876
$\Sigma_{22}$	0.0012071	0.0016876
$\Sigma_{33}$	0.0034016	0.0064436
$\Sigma_{44}$	0.0120245	0.0235547
$\Sigma_{31}$	-0.0019784	-0.0004759
$\Sigma_{55}$	0.0029865	0.0051924
$\Sigma_{66}$	0.0118936	0.0213646
$\Sigma_{77}$	0.0187428	0.0366932
$\Sigma_{57}$	0.0015374	0.0025835
$\Sigma_{88}$	0.0059449	0.0108410

TABLE III

Symmetrized mean-square amplitude matrices in  $\text{\AA}^2$  for antimony pentachloride

Element	Symmetrized mean-square amplitude matrix	
	T=0	T= 298°K
$\Sigma_{11}$	0.0015491	0.0026933
$\Sigma_{22}$	0.0013360	0.0020737
$\Sigma_{33}$	0.0024696	0.0106235
$\Sigma_{44}$	0.0075013	0.0128476
$\Sigma_{34}$	0	0
$\Sigma_{55}$	0.0023546	0.0084436
$\Sigma_{66}$	0.0092475	0.0167894
$\Sigma_{77}$	0.0140328	0.0279458
$\Sigma_{57}$	0.0011374	0.0023647
$\Sigma_{88}$	0.0100275	0.0414265

TABLE IV

Symmetrized mean-square amplitude matrices in  $\text{\AA}^2$  for niobium pentachloride

Element	Symmetrized mean-square amplitude matrix	
	T=0	T= 298°K
$\Sigma_{11}$	0.0013397	0.0020809
$\Sigma_{22}$	0.0011543	0.0015157
$\Sigma_{33}$	0.0024576	0.0043286
$\Sigma_{44}$	0.0069034	0.0129874
$\Sigma_{34}$	-0.0011565	-0.0016437
$\Sigma_{55}$	0.0023546	0.0036136
$\Sigma_{66}$	0.0064624	0.0119645
$\Sigma_{77}$	0.0092845	0.0194874
$\Sigma_{57}$	0.0009834	0.0018362
$\Sigma_{88}$	0.0108795	0.0449467

TABLE V

Mean-square amplitude quantities in Å<sup>2</sup> for phosphorous pentachloride

Symbol	Mean-square amplitude quantity T = 0	Mean-square amplitude quantity T = 298°K
$\sigma_r$	0.0023934	0.0040241
$\sigma_{rr}$	-0.0005931	-0.0011683
$\sigma_d$	0.0023044	0.0040656
$\sigma_{dl}$	-0.0010973	-0.0023780
$\sigma_\theta$	0.0079291	0.0142431
$\sigma_{\theta\theta}$	-0.0039645	-0.0071215
$\sigma_\varphi$	0.0123018	0.0238880
$\sigma_{\varphi\varphi}$	0.0000934	0.0005743
$\sigma'_{\varphi\varphi}$	-0.0000420	0.0001206
$\sigma''_{\varphi\varphi}$	-0.0062050	-0.0123517
$\sigma_{d\varphi}$	-0.0005712	-0.0001374
$\sigma'_{d\varphi}$	0.0005712	0.0001374
$\sigma_{r\varphi}$	0.0007247	0.0012179
$\sigma'_{r\varphi}$	-0.0003624	-0.0006090
$\sigma_p$	0.0046827	0.0078446
$\sigma_{pp}$	-0.0005308	-0.0013909
$\sigma_q$	0.0076190	0.0150106
$\sigma_{qq}$	-0.0011333	-0.0012960
$\sigma'_{qq}$	0.0016256	0.0020884
$\sigma''_{qq}$	-0.0029137	-0.0058904
$\sigma_{pq}$	0.0013244	0.0021220
$\sigma'_{pq}$	-0.0011704	-0.0021769

TABLE VI

Mean-square amplitude quantities in  $\text{\AA}^2$  for antimony pentachloride

Symbol	Mean-square amplitude quantity	
	T = 0	T = 298°K
$\sigma_r$	0.0020861	0.0065268
$\sigma_{rr}$	-0.0002685	-0.0019168
$\sigma_d$	0.0019028	0.0063486
$\sigma_{dd}$	-0.0005668	-0.0042749
$\sigma_u$	0.0061650	0.0111929
$\sigma_{uu}$	-0.0030825	-0.0055965
$\sigma_\varphi$	0.0102292	0.0252125
$\sigma_{\varphi\varphi}$	-0.0008740	-0.0065820
$\sigma'_{\varphi\varphi}$	-0.0018610	-0.0094735
$\sigma''_{\varphi\varphi}$	-0.0028766	-0.0001582
$\sigma_{d\varphi}$	0	0.0011502
$\sigma'_{d\varphi}$	0	-0.0011502
$\sigma_{r\varphi}$	0.0005362	0.0011147
$\sigma'_{r\varphi}$	-0.0002681	-0.0005574
$\sigma_p$	0.0042677	0.0097133
$\sigma_{pp}$	0.0001897	-0.0008167
$\sigma_q$	0.0071659	0.0213352
$\sigma_{qq}$	-0.0008311	-0.0019017
$\sigma'_{qq}$	-0.0006617	-0.0022270
$\sigma''_{qq}$	-0.0016446	-0.0047507
$\sigma_{pq}$	0.0012773	0.0031645
$\sigma'_{pq}$	-0.0008651	-0.0034625

TABLE VII

Mean-square amplitude quantities in  $\text{\AA}^2$  for niobium pentachloride

Symbol	Mean-square amplitude quantity	
	T = 0	T = 298°K
$\sigma_r$	0.0020163	0.0031027
$\sigma_{rr}$	-0.0003383	-0.0005109
$\sigma_{il}$	0.0018060	0.0029222
$\sigma_{ill}$	-0.0006517	-0.0014065
$\sigma_{..}$	0.0043083	0.0119645
$\sigma_{..}$	-0.0021541	-0.0039882
$\sigma_\varphi$	0.0083143	0.0226038
$\sigma_{\varphi\varphi}$	-0.0021247	-0.0096117
$\sigma'_{\varphi\varphi}$	-0.0017677	-0.0096138
$\sigma''_{\varphi\varphi}$	-0.0013271	0.0031179
$\sigma_{d\varphi}$	-0.0003339	-0.0004745
$\sigma'_{d\varphi}$	0.0003339	0.0004745
$\sigma_{r\varphi}$	0.0004636	0.0008656
$\sigma'_{r\varphi}$	-0.0002378	-0.0004328
$\sigma_p$	0.0035941	0.0058818
$\sigma_{pp}$	0.0002124	0.0001804
$\sigma_q$	0.0059769	0.0152248
$\sigma_{qq}$	-0.0009370	-0.0039889
$\sigma'_{qq}$	-0.0001613	-0.0031374
$\sigma_{qq''}$	-0.0008352	0.0001223
$\sigma_{pq}$	0.0011695	0.0018523
$\sigma'_{pq}$	-0.0006983	-0.0011559

TABLE VIII

Mean amplitudes of vibration in Å for some trigonal bipyramidal pentachlorides

Molecule	Distance	Mean amplitude of vibration	
		T = 0	T = 298°K
PCl <sub>5</sub>	X—Y(equatorial)	0.0489	0.0634
	X—Y(axial)	0.0480	0.0638
	Y(equatorial)—Y(equatorial)	0.0684	0.0886
	Y(equatorial)—Y(axial)	0.0873	0.1225
SbCl <sub>5</sub>	X—Y(equatorial)	0.0458	0.0808
	X—Y(axial)	0.0436	0.0797
	Y(equatorial)—Y(equatorial)	0.0653	0.0986
	Y(equatorial)—Y(axial)	0.0847	0.1461
NbCl <sub>5</sub>	X—Y(equatorial)	0.0449	0.0557
	X—Y(axial)	0.0425	0.0541
	Y(equatorial)—Y(equatorial)	0.0600	0.0767
	Y(equatorial)—Y(axial)	0.0773	0.1234

## ACKNOWLEDGMENT

This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is made to the donors of said Fund.

## REFERENCES

- Cyvin, S. J., 1959, *Spectrochimica Acta*, **15**, 828.  
 Gaunt, J. and Ainscough, J. B., 1957, *Spectrochimica Acta*, **10**, 52.  
 Haarhoff, P. C. and Pistorius, G. W. F. T., 1959, *Zeitschrift fuer Naturforschung*, **14**, 972.  
 Keirz, T. and Stricks, W., 1937, *Monatsh, Chem.*, **71**, 1.  
 Krishnamurthi, P., 1930, *Ind. J. Phys.*, **5**, 116.  
 Moureu, H., Magat, M. and Wetroff, G., 1937, *C. R. Acad. Sci. Paris*, **205**, 276.  
 Moureu, H., Magat, M. and Wetroff, G., 1938, *Pro. Indian. Acad. Sci.*, **8A**, 356.

- Mourou, H., Magat, M. and Sue, P., (1947-1948), Contributions a l'Etude de la structure Moléculaire, Victor Henri Commemorative Vol, P 125, Desoer, Liez.
- Nagarajan, G., 1962, *Bull. Soc. Chim. Belg.* **71**, 324.
- Ohlberg, S., 1954, *Acta Cryst.* **7**, 640.
- Pauling, L., "Nature of Chemical bond," (Cornell University Press, Ithaca), 1942, Second edition, Page 109.
- Ruault, M., 1940, *Ann. Phys.* **14**, 78.
- Sargent and Schomaker, V., 1941, *J. Chem. Phys.* **9**, 403.
- Siebert, G., 1962, H., 1951, *Z. anorg.u. allgem. Chem.* **265**, 303.
- Skinner, H. A. and Sutton, L. E., 1940, *Trans. Farad. Soc.* **36**, 668.
- Wilmshurst, J. K. and Bernstein, H. J., 1957, *J. Chem. Phys.* **27**, 661.
- Wilmshurst, J. K., 1960, *J. Mol. Spectroscopy.* **5**, 343.
- Wilson, E. B. Jr., 1939 and 1941, *J. Chem. Phys.* **7**, 1041; **9**, 76.